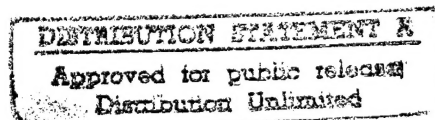**2nd Interim Report, Contract N 68171-95-C-9086**

Title: Isodisperse Telechelic Polymers and their Polyurethane

Derivatives

In this part of the Contract three other HTPBD samples have been prepared, characterised by the following molecular weights:

No.4.   Nominal $\overline{M}_n$ = 1000

Experimental: $\overline{M}_n$ = 1245

Polydispersity: $\overline{M}_w/\overline{M}_n$ = 1,34

No.5.   Nominal $\overline{M}_n$ = 1500

Experimental: $\overline{M}_n$ = 1552

Polydispersity: $\overline{M}_w/\overline{M}_n$ = 1,34

No.6.   Nominal $\overline{M}_n$ = 10000

Experimental: $\overline{M}_n$ = 10800

Polydispersity: $\overline{M}_w/\overline{M}_n$ = 1,95

The details of the polymerization recipe of the individual samples were given in our previous 2nd Interim Report (December 21, 1995. Contract No. N68171-95-C-9086). The samples were sent by air mail on January 25, 1996. The structures of the samples were characterised by FT-IR, ^{1}H-NMR and GPC investigations. The measurements are given graphically, their evaluations are summarised in the Table 1.

The FT-IR spectra of the samples were recorded by a Bomem MB-100 spectrophotometer. Figure 1 shows the FT-IR spectra of the samples HTPBD-1000, HTPBD-1500 and HTPBD-10000.

The percentage of the 1,4-trans, 1,2-, and 1,4-cis-linkages in the poly-butadiene chain was calculated from the respective absorption at

965.7 cm^{-1}, 911.7 cm^{-1} and 722.7 cm^{-1}. We have to emphasise that the weak absorption of the 1,4-cis units at 720-740 cm^{-1} can cause some uncertainty in the calculation.

The three spectra show difference only in two regions. Because of the high molecular weight of the HTPBD-10000 the OH endgroup concentration is very low and their absorption at 3200-3600 cm^{-1} can not be seen. For the same reason the absorption of the -C≡N group of the initiator fragments at 2218.7 cm^{-1} appears only in the spectra of the HTPBD-1000 and HTPBD-1500. In case of these polymers the intensity of the absorpiton of the -OH and -C≡N groups is also effected by the respective groups of the recombination product of the ACP initiator remained in the polymers.

Table 1. Microstructure of HTPBD samples based on FT-IR and ^{1}H-NMR measurements

Sample	Microstructure by				
	FT-IR			^{1}H-NMR	
	1,2 bond	1,4 bond cis	1,4 bond trans	1,2 bond	1,4 bond
	%			%	
HTPBD-1000	11.1	35.2	53.6	14.7	85.3
HTPBD-1500	11.1	31.0	57.9	14.7	85.3
HTPBD-10000	12.6	28.3	59.2	14.0	86

The microstructure of the polymers determined by the FT-IR measurements were verified by the data based on the ^{1}H-NMR measurements (see Table 1).

Figures 2-4 show the ^{1}H-NMR spectra of the samples. The assignation of the peaks were given in our 1st Interim Report (November 10. 1995.) Since HTPBD-1000 and HTPBD-1500 were synthesised using only ACP initiator the resonance at 4.08 ppm correlated to the protons in the HO-$\underline{CH_2}$-CH=CH-CH_2-group (end group in case of H_2O_2-initiation) can not be seen in the spectra of the polymers above.

Figures 5-7 show the molecular weight distribution of the three polymers. It is noteworthy that the molecular weight distribution of samples No.4 and No.5 is lower even than the theoretical value ($\overline{M}_w/\overline{M}_n = 1.5$). This is favourable in respect of the physical-mechanical properties of the PU rubbers prepared with these samples since oligomers with mono dispersity would give the best rubber according to the elasticity theory.

At the same time the question arises that what would be the interpretation of the polydispersity lower than the theoretical one.

We have two explanations, an experimental and a theoretical one.

According to the experimental explanation the calibration curve of the GPC is inaccurate in the low molecular weight range ($M_n < 1000$). Thus, the molecular weight distribution calculated by means of such calibration curve will be inaccurate to the same extent as the calibration curve itself. So, the cause of the deviation according to this assumption is the imperfectness in the evaluation of the calibration curve. A further possible explanation is that during the samples preparation the very low molecular weight portion of the polymer is partially lost causing narrowing of the molecular weight distribution.

The <u>theoretical explanation</u> is based on the fundamental of the distribution functions. Strictly speaking, the rate constants of the elemental reactions in the polymerization are size-dependent:

$$R_i^{\cdot} + M \rightarrow R_i^{\cdot} \qquad (k_{2,i})$$

$$(1)$$

or

$$R_i^{\cdot} + R_j^{\cdot} \rightarrow P_{i+j} \quad (k_{4,ij})$$

$$(2)$$

where R· stands for the growing active center and P for the polymer molecule formed.

That is the numerical value of $k_{2,i}$ and $k_{4,ij}$ depends on the size of $R_i^{\cdot}$ and $R_j^{\cdot}$ (practically the degree of the polymerization).

As a reminder: according to the collision theory (the simplest reaction kinetic theory) the collision number (z) (that is the preexponential coefficient of the rate constant) is the function of the molecular weight of the reaction partners.

In the today practice we assume that $k_{2,i}$ and $k_{4,ij}$ is independent of the size (molecular weight) of the active center:

$$k_{2,i} = k_2 = \text{const.}$$

$$(3)$$

$$k_{4,ij} = k_4 = \text{const.}$$

$$(4)$$

However, we must keep in mind that the above assumption serving our convenience during the calculation is not valid under any circumstances like a theoretical thesis.

Research in the past decades primarily on the field of telomerization has proved that in the low molecular weight range:

$$1 \leq i,j \leq 20$$

$$(5)$$

the above assumption is applicable only with restriction or not at all since the experimental results deviate considerably from the distribution functions calculated by the theory.

To determine which explanation is valid in our case, more designed experimental work must be done. This work may be accomplished during our planned cooperation in 1996.

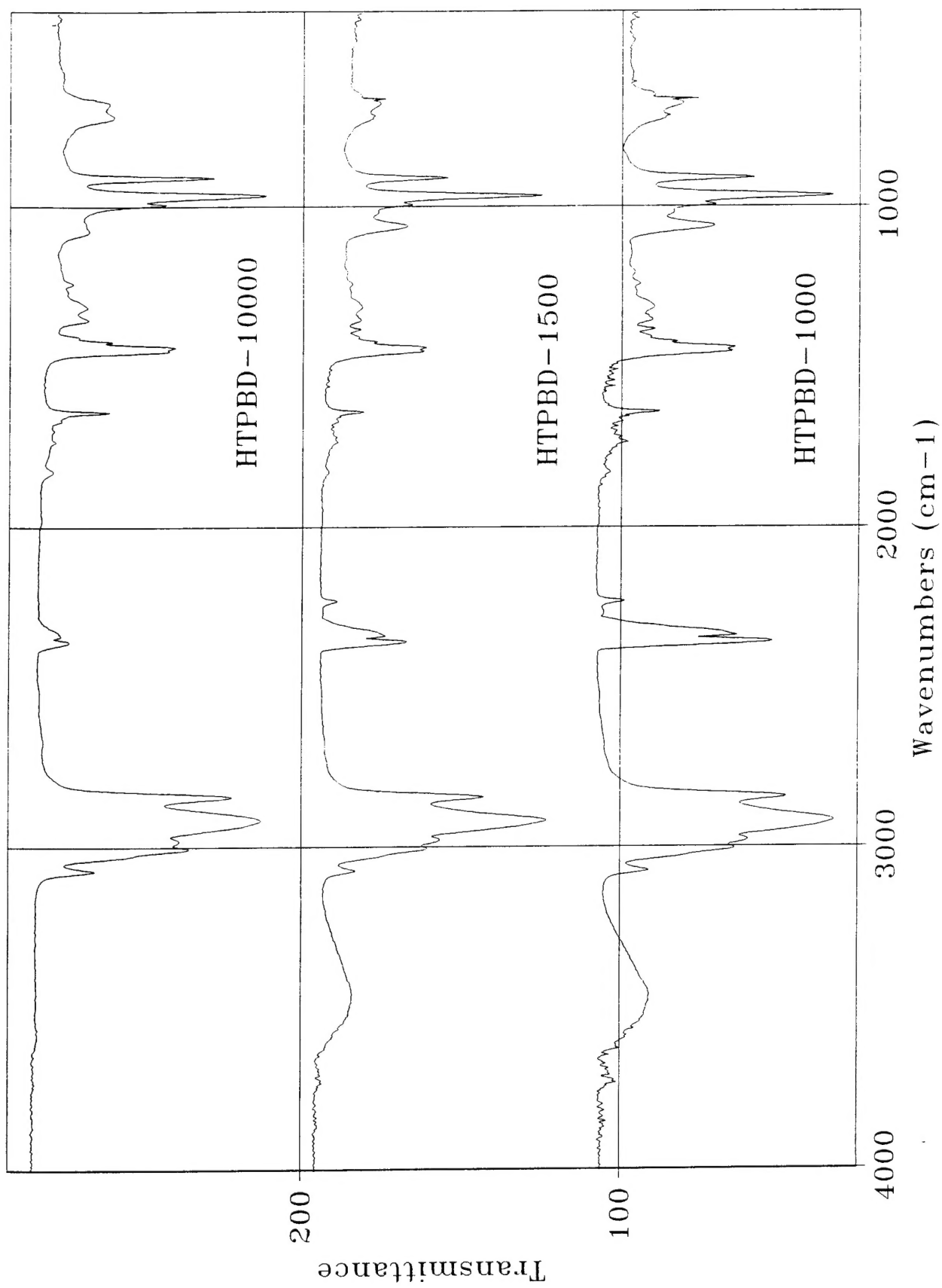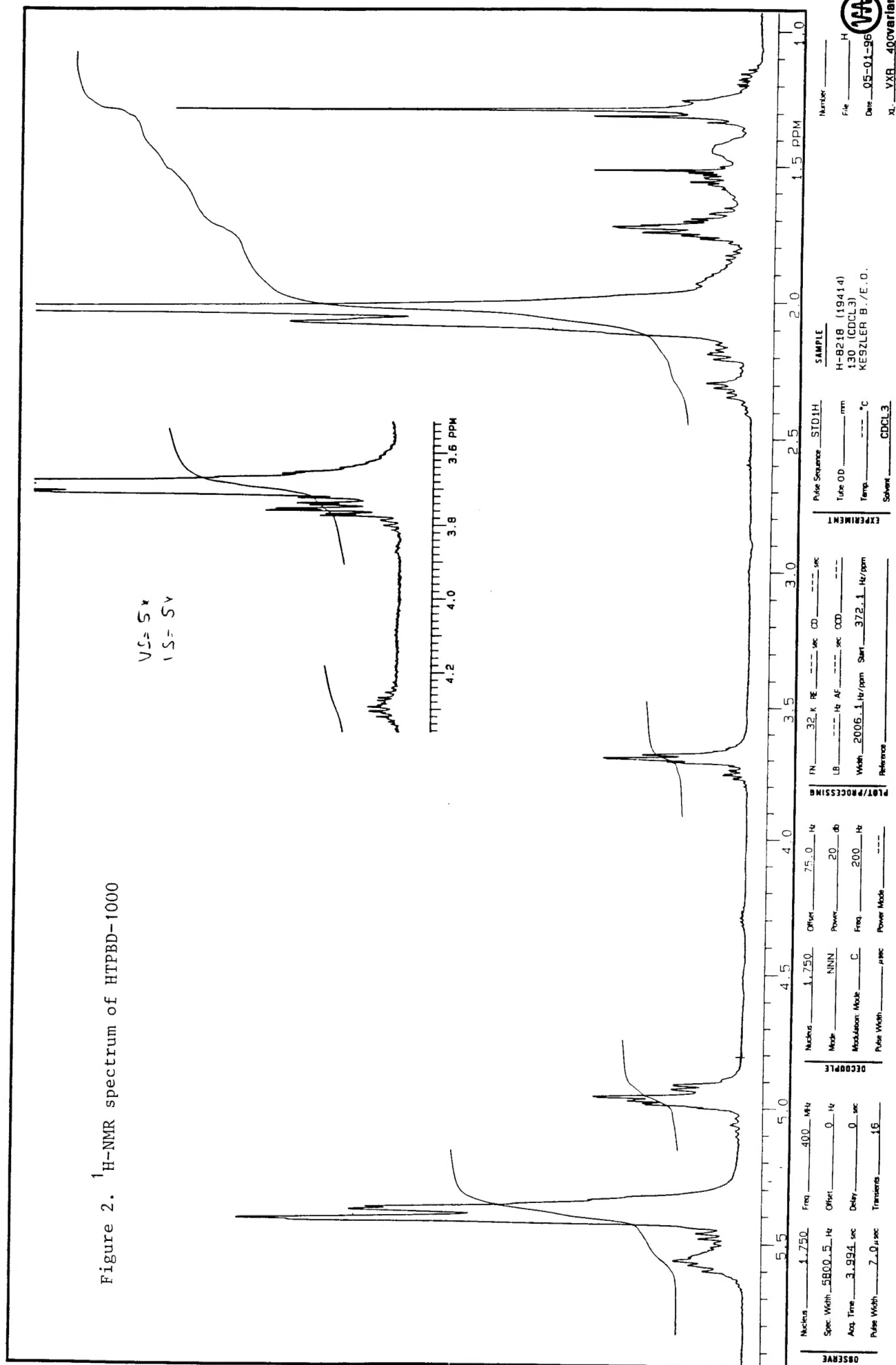At this point we can conclude that the lower molecular weight distribution is even favourable for the preparation of the PU rubbers.

Figure 1. FT-IR Spectra of HTPBD samples.

HTPBD-10000

HTPBD-1500

HTPBD-1000

Transmittance

200

100

Wavenumbers (cm−1)

4000   3000   2000   1000

Figure 2. ^{1}H-NMR spectrum of HTPBD-1000

Figure 3. ^{1}H-NMR spectrum of HTPBD-1500

VS = 5x
IS = 5x
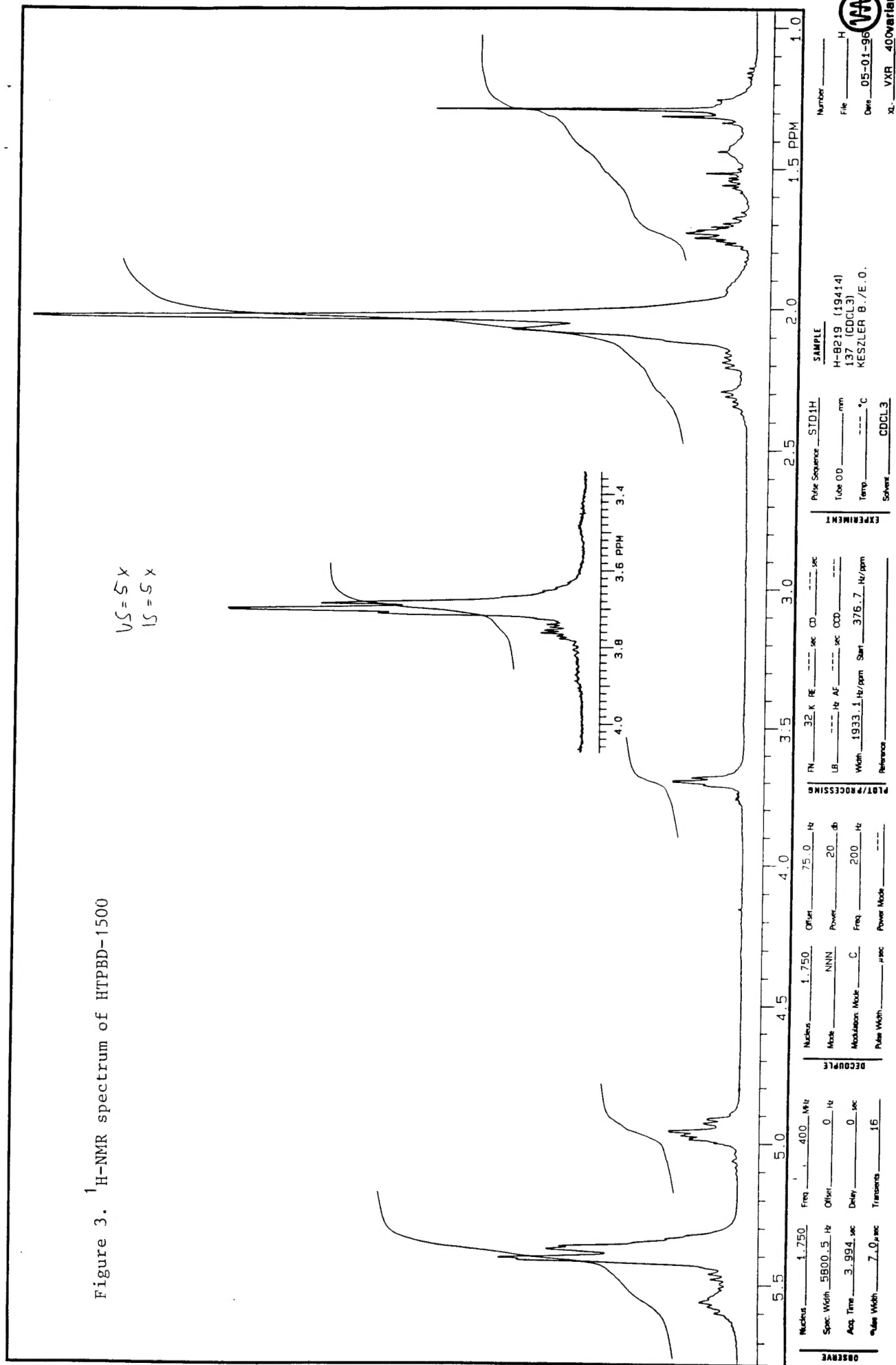
Figure 4. ^{1}H-NMR spectrum of HTPBD-10000
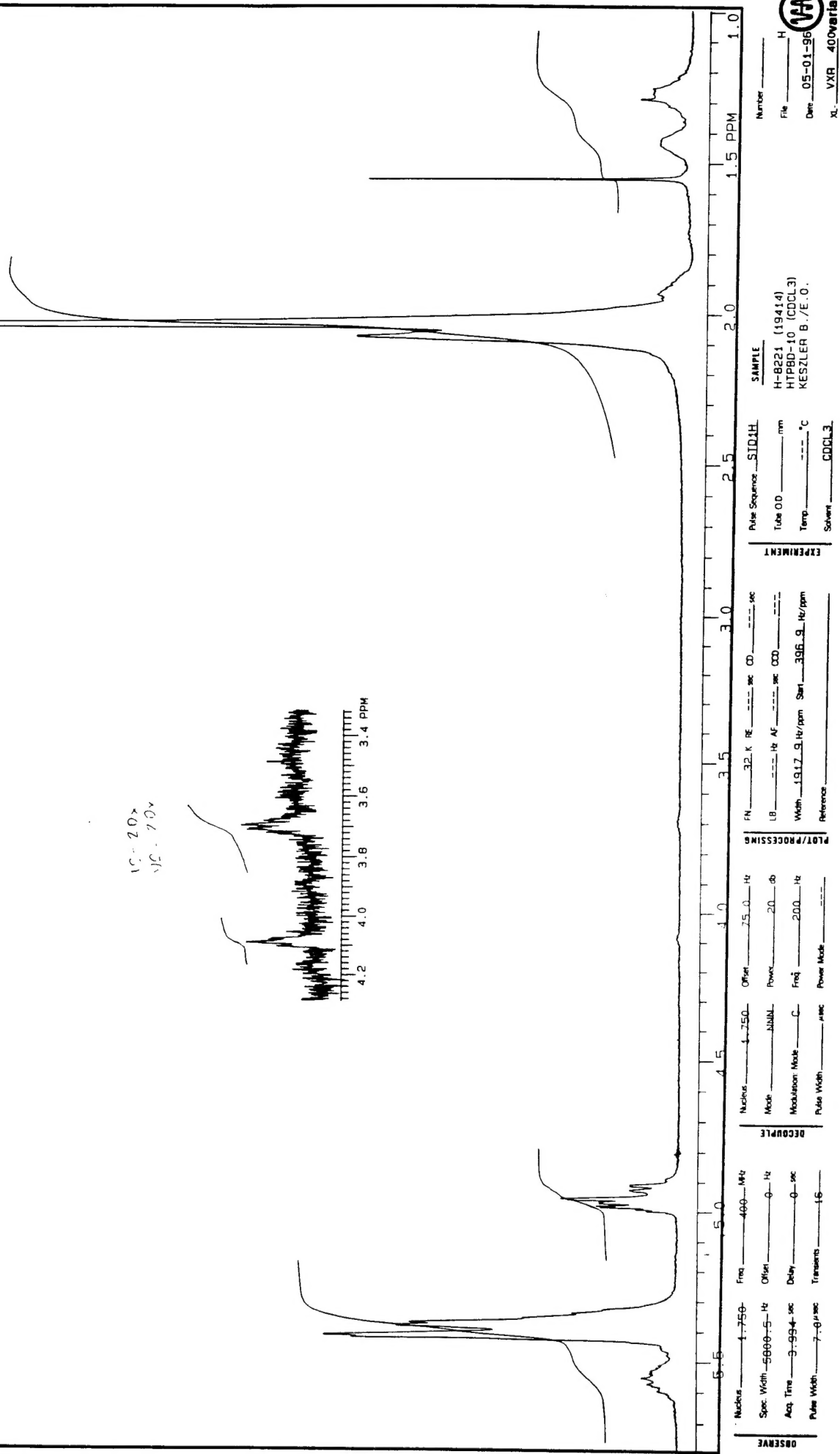
Figure 5: Molecular weight distribution of HTPBD-1000
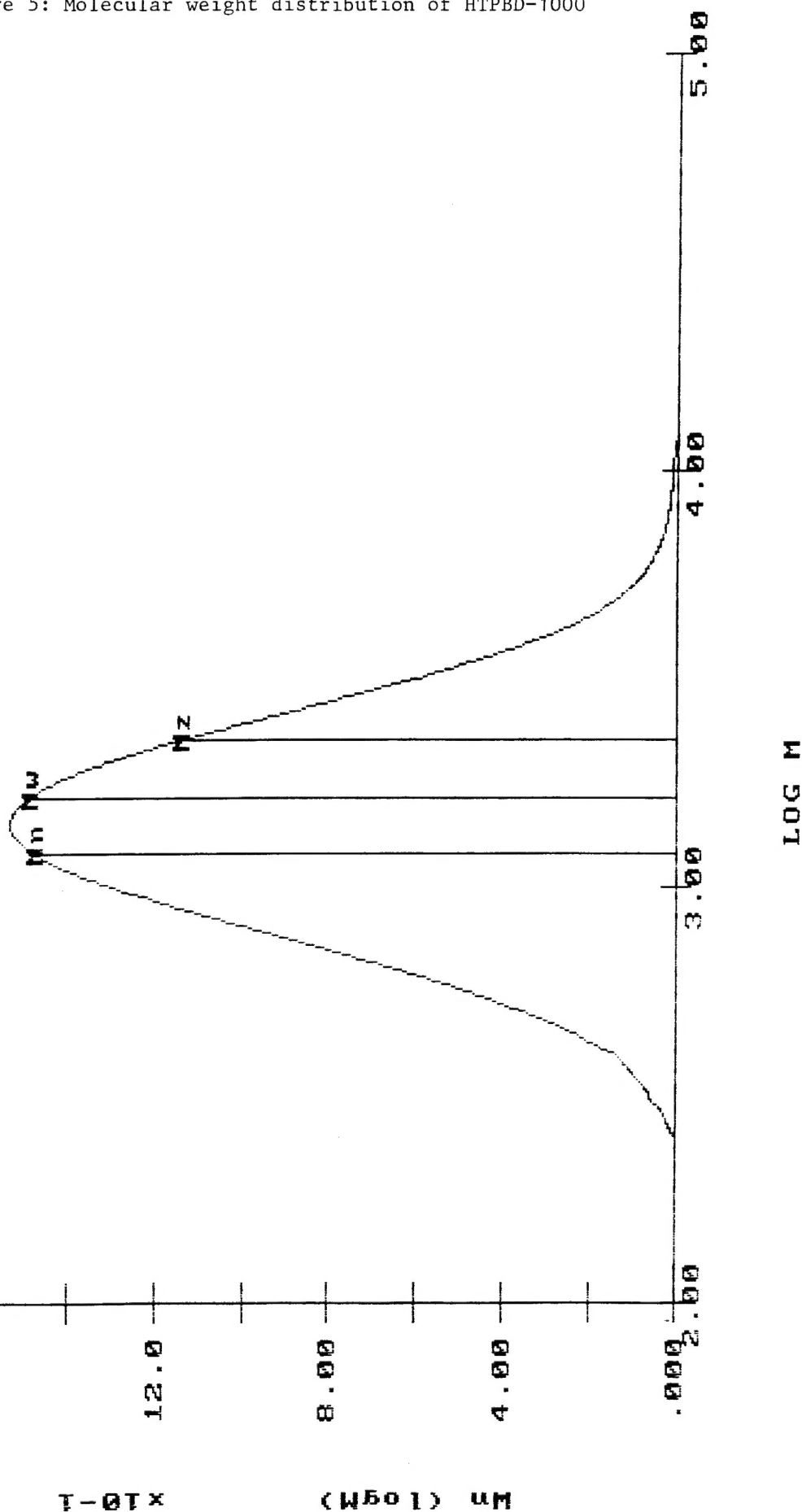
MOLECULAR WEIGHT DISTRIBUTION

Mn= 1.25E3

Mw= 1.67E3

Mz= 2.25E3

Figure 6: Molecular weight distribution of HTPBD-1500

Figure 7: Molecular weight distribution of HTPBD-10000

MOLECULAR WEIGHT DISTRIBUTION
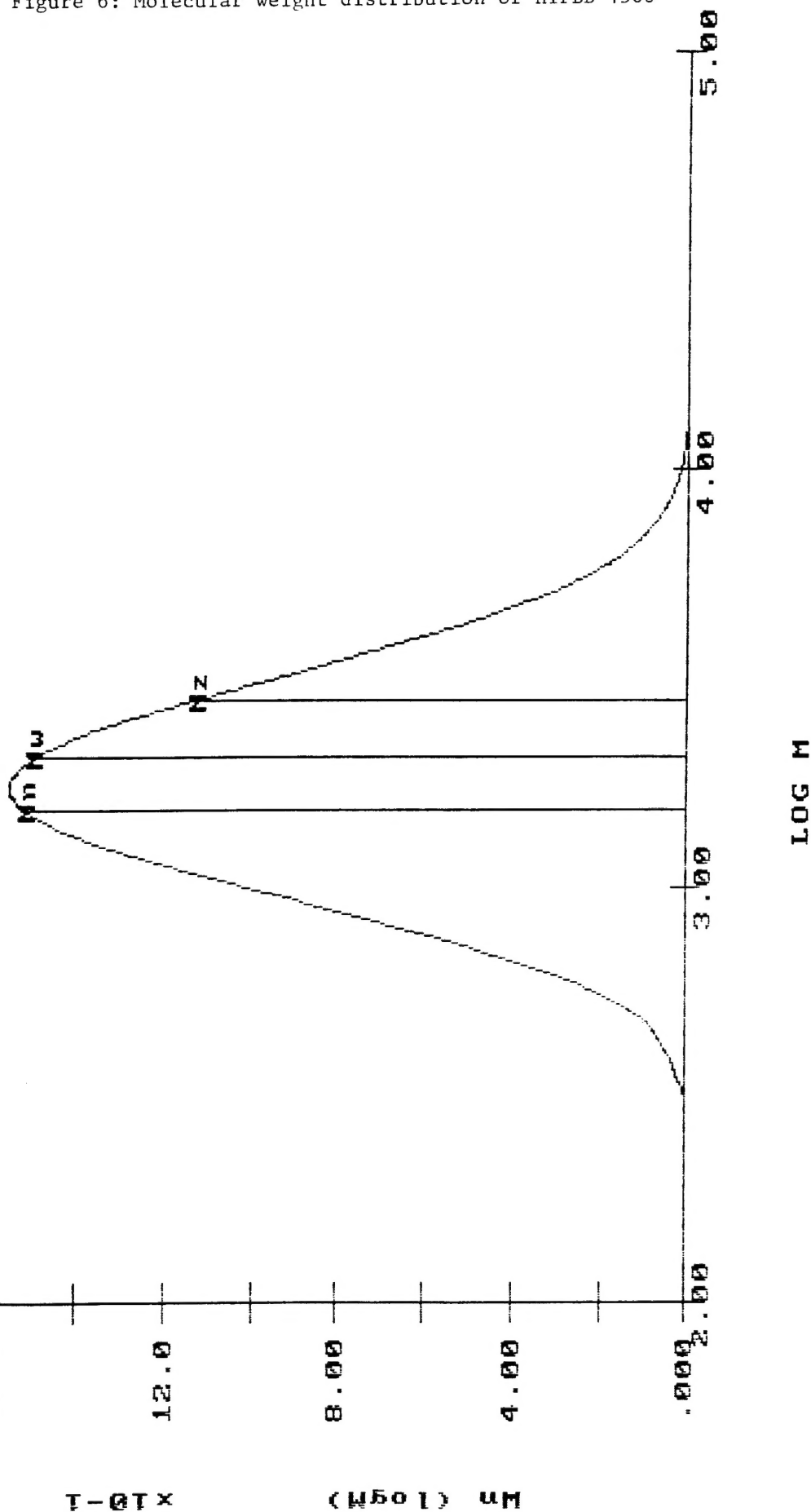
VISCOTEK CORP.   UCHL 4.05   ENDED: 01/03/96 14:06
FILENAME: x6a   RUN ID: 96/1 polibut. X-6

Mn= 1.08E4

Mw= 2.10E4

Mz= 3.78E4

Mn (logM)   x10-1

LOG M

15.0

12.0

9.00

6.00

3.00

.000

2.00   3.00   4.00   5.00   6.00

Mn   Mw   Mz